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The Metal in the Polarisable Interface Coupling With the Solvent Phase

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Abstract

A quantum mechanical treatment of the conduction electrons of a metal in a polarisable interface shows that they can make an appreciable contribution to the electrical capacitance. Results for six metals are given, showing how differences in metal properties account qualitatively for experimentally observed differences in interfacial capacities, when the solvent is replaced by a dielectric film. To justify the neglect of solvent structure when metal properties are treated, the coupling between metal and solvent is discussed for orientable point solvent dipoles, and for a representation of the solvent polarisation by a pair of charged planes. The electron profile affects the polarisation of the solvent near the point of zero charge, but the solvent structure has an almost negligible effect on the metal contribution to the capacity. One parameter in our model, the distance from metal ions to the first solvent layer, can be expected to vary as the interface is charged, due to changed bonding. Coupling by such an effect can be quite important, and severely decreases the variation of metal capacity with charge.

Introduction

Models for the ideally polarisable electrode in the absence of specific adsorption agree in dividing the interface into an inner compact layer and an outer diffuse layer and in considering that the former is constituted by the surface of a metal covered by a layer of solvent molecules [1]. The surface charge density of the solution σ_s is supposed to be localised at the outside of the solvent layer and that of the metal σ_M ($\sigma_M = -\sigma_s$) in a structureless layer. The electric field associated with σ_M deforms and orients the solvent molecules. The deformation is generally characterized by a permittivity ϵ_1 which is assumed to be independent of σ_M ; the resulting electrical capacity, denoted by $C(\text{ion})$, is equal to d/ϵ_1 , where d is of the size of the diameter of a solvent molecule. The orientation of solvent molecules gives rise to a charge-dependent potential drop $g^S(\text{dip})$, and thus to a capacity $C^S(\text{dip}) = \partial\sigma_M/\partial g^2(\text{dip})$. The total capacity is written

$$1/C = 1/C(\text{ion}) - 1/C^S(\text{dip}) \quad (1)$$

[End of page 25]

The nature of the metal appears only through solvent adsorption energies which favor certain orientations, thus affecting $g^S(\text{dip})$ and $C^S(\text{dip})$. A direct contribution of the metal particles (ions and electrons) has been suggested, and estimated crudely, although some recent research has been aimed at a quantitative calculation [2-6].

We have given a first estimation of the contribution of the metal to the electrical potential difference [3] and the capacity at the point of zero charge [4]. Since the objective was to establish whether the metal contribution could be noticeable compared with the experimental values of these quantities, a particularly simple representation was chosen for the solution. Only the deformation polarisation, by way of ϵ_1 , was included, and we assumed that $C^M(\text{dip})$ and $C^S(\text{dip})$ could be calculated separately. Our calculations showed that the direct contribution of the metal could be important, although much weaker than that suggested by Rice [7] or that calculated more recently by Kuklin [2]. Therefore, we are now led to consider more precisely the coupling between $C^M(\text{dip})$ and $C^S(\text{dip})$.

In the present work, we examine the possible effect of more sophisticated models of the solution. In section (1) we review our model and give new results for a series of metals. In Section (2), point dipoles are introduced for $C^S(\text{dip})$ and their influence on $C^M(\text{dip})$ is studied. We also consider the replacement of point dipoles by separated charges. In section (3) we show the effect on $C^M(\text{dip})$ of an overall displacement of the first solvent layer relative to the jellium. Finally, the implications of results for future theoretical work on the interface are indicated.

(1) Model for Calculation of Electronic Properties

A detailed description of the model has already been given [3,4], so that only several main points are discussed here. The uniformly distributed metal ions (jellium) interact with the electrons by way of a Heine-Animalu pseudopotential. On the solution side of the interface, the interaction of the electrons with the solvent molecules is represented by a repulsive pseudopotential (Harrison point ion model) and a dielectric film of permittivity ϵ_1 , corresponding to the capacity $C(\text{ion})$ described above. The parameters of the model are: the distance between the dielectric film and the jellium edge d_1 , the thickness of the film $d_2 - d_1$, the permittivity ϵ_1 of the film, and ϵ_2 , the permittivity of the medium beyond the film (the value of the last is not important). We have taken $d_2 - d_1 = 0.3$ nm, $\epsilon_1 = 6$, and $\epsilon_2 = 78$ for all the metals, whereas for d_1 , which depends on the metal, we have used the crystallographic radius. The electron profile is taken as

$$n(z) = n \left(1 - \frac{e^{\alpha(z-z_0)}}{1 + \alpha/\beta} \right) \quad \text{for } z \leq z_0 \quad (2)$$

$$= n \frac{e^{-\beta(z-z_0)}}{1 + \beta/\alpha} \quad \text{for } z > z_0$$

with n the electron density of bulk metal and $z_0 = \alpha^{-1} - \beta^{-1} - \sigma_M/n$. The parameters of the pseudopotential have been previously given [4], [End of page 26]

TABLE 1
Values of d_1 and n used for calculations on six metals, with resulting capacities

Metal	Elec. dens. n in a.u.	d_1 /nm	$C^*/\mu\text{F cm}^{-2}^a$	$C^{\text{exp}}/\mu\text{F cm}^{-2}$	$C^{\text{calc}}/\mu\text{F cm}^{-2}$
Hg	0.01267	0.212	11	28	21
Cd	0.01381	0.195	13	52	26
Pb	0.01966	0.159	15	40	40
Zn	0.01961	0.157	17	100	50
In	0.01711	0.174	17	60	50
Ga	0.02283	0.117	21	135	114

$$^a C^* = [1/C(\text{ion}) + 1/C^M(\text{dip})]^{-1}.$$

For a given value of the metal surface charge σ_M we calculate the surface energy U_{s0} of the electron gas and minimize it with respect to α and β . Then, by integration of the Poisson equation we calculate all the electrical properties as functions of σ_M . In Table 1 we give the values of d_1 and n used for calculations on six metals, and C^* , the inverse of $C(\text{ion})^{-1} + C^M(\text{dip})^{-1}$, resulting from these calculations. The quantity $C(\text{ion})$ is $4\pi(d_2 - d_1)/c_1 = 17$ $\mu\text{F/cm}^2$. If one uses the same value of $C^S(\text{dip})$ for the metals Hg, Ga, and In, it is clear that one has $C(\text{Hg}) < C(\text{In}) < C(\text{Ga})$, which is in accord with experimental values. If one further chooses the reasonable value of 25 $\mu\text{F/cm}^2$ for $C^S(\text{dip})$, one may find calculated capacities quite close to the experimental values given by [8]. It is to be noted that differences in capacities between metals are already qualitatively predicted by our model of the metal without invoking differences in the strength of solvent adsorption. A correct model of the interface should probably take both aspects into account.

In order to be able to relate differences in $C^M(\text{dip})$ to differences in experimental capacities, we have assumed inverse capacitances are additive, i.e. that the interface behaves as several capacitances in series. This assumption also permits us to use an oversimplified model for the electrolyte part of the interface when we perform calculations on the metal part. We now examine the coupling between $C^M(\text{dip})$ and $C^S(\text{dip})$ to see how far this is justified, limiting ourselves to the case of mercury.

(2) Metal-Dipolar Coupling

The solvent molecules in many contemporary theories of the interface are represented by point dipoles. If these are introduced into the dielectric film, there is a new contribution ΔU_s to the surface energy which, by elementary electrostatics, may be written

$$\Delta U_s = -4\pi \frac{\langle P \rangle}{\epsilon_1} \left[\sigma_M + \frac{\alpha n}{\beta(\alpha + \beta)} e^{\beta(z_0 - 1/2(d_1 + d_2))} \right] \quad (3)$$

where the dipole layer is at the center of the dielectric film, and $\langle P \rangle$ is the mean polarisation (dipole moment per unit area) of the dipoles. According to eqn. (3), the [End of page 27] effect of the electrons is that $\langle P \rangle$ interacts with the field of an effective charge $\sigma_M + \delta\sigma$ where

$$\delta\sigma = \frac{\alpha n}{\beta(\alpha + \beta)} e^{\beta(z_0 - 1/2(d_1 + d_2))} \quad (4)$$

which simply represents minus the total electronic charge found on the electrolyte side of the plane at $1/2(d_1 + d_2)$. In order to calculate $\langle P \rangle$ as a function of the field, for example according to the model of Parsons [9], the field $E = 4\pi\sigma_M/\epsilon_1$ must be replaced by the effective field

$$E_{\text{eff}} = (4\pi/\epsilon_1)(\sigma_M + \delta\sigma)$$

As far as the electron profile is concerned, its parameters are determined by minimization of $U_{s0} + \Delta U_s$.

For the one-parameter profile obtained by taking $\alpha = \beta$ in eqn. (2), the effect of minimizing $U_{s0} + \Delta U_s$ rather than U_{s0} alone is shown in Table 2. We have calculated $\langle P \rangle$ using the model and parameters of Parsons' model [9]. In Table 2, α_0 is obtained for $\Delta U_s = 0$; one sees that the difference between α and α_0 is extremely small, except for the most negative values of σ_M . The same is true when α and β are varied independently: for example, at $\sigma_M = -16$ we find $\alpha = 0.784$ and $\beta = 0.774$ without dipoles, and $\alpha = 0.754$ and $\beta = 0.829$ with dipoles. The potential drop changes only from 3.627 to 3.563 V. The effect on the capacitance C^* is shown in Table 3. We see that calculations of metal capacity $C^M(\text{dip})$ may be performed without considering the solvent polarisation. This holds regardless of the point dipole model used, since the reason for the smallness of the coupling is that the solvent dipoles are in a region of extremely low electron density, so their effect on the electrons is very small.

As an improvement on point dipoles, one may imagine that the origin of the polarisation $\langle P \rangle$ is in the orientation of molecules, each of which carries partial charges $+\lambda e$ and $-\lambda e$ separated by a distance l . It is easy to show that the modification of the surface energy is now given by

$$\Delta U_s = -\frac{4\pi\langle P \rangle}{\epsilon_1} \left[\sigma_M + \frac{n\alpha}{\beta(\alpha + \beta)} e^{\beta(z_0 - (d_1 + d_2)/2)} \frac{e^{\beta l/2} - e^{-\beta l/2}}{\beta l} \right] \quad (5)$$

TABLE 2
Effect of minimizing $U_{s0} + \Delta U_s$ rather than U_{s0} alone

$\sigma_M/\mu\text{C cm}^{-2}$	α_0/nm^{-1}	α/nm^{-1}	$\delta\sigma/\mu\text{C cm}^{-2}$
16	11.18	11.20	0.10
8	10.21	10.21	0.20
4	9.752	9.750	0.28
0	9.313	9.311	0.39
-4	8.896	8.896	0.52
-8	8.503	8.513	0.69
-16	7.787	7.852	1.12

[End of page 28]

TABLE 3

Effect of changing d_1 on capacity C^* ^a

$\sigma_M/\mu\text{F cm}^{-2}$	$C^*/\mu\text{F cm}^{-2}$		
	$\mu = 0$ ^b	$\mu = 0$	$\mu = R_c/80$
18	7.16	7.14	11.89
14	7.64	7.62	11.30
10	8.19	8.16	10.98
6	8.76	8.79	10.68
3	9.22	9.30	10.49
1	9.51	9.66	10.46
0	9.66	9.85	10.42
-1	9.82	10.05	10.40
-3	10.16	10.53	10.39
-6	10.73	11.17	10.47
-10	11.56	12.16	10.67
-14	12.46	13.28	11.43
-18	13.42	14.93	12.35

^a $(C^*)^{-1} = C(\text{ion})^{-1} + C^M(\text{dip})^{-1}$.^b Calculated by minimizing energies including Parsons-model polarisation, to show it may be neglected in determining metal properties.

Letting I approach zero, we recover point dipoles, and eqn. (5) becomes eqn. (3). For water, we estimate I as the perpendicular distance from the oxygen to the midpoint of the H-H line, i.e. 0.0578 nm. Since Bl is about unity, the term $(e^{Bl/2} - e^{-Bl/2})/Bl$ does not differ much from 1, so that, taking values of (P) similar to those of Parsons' model, we find that the second term of eqn. (5) is of the same size as for point dipoles. Thus the conclusion that it is unimportant is unchanged.

These results confirm the validity of our assumption that the behavior of the metal electrons is calculable independently of the model used for the solvent. On the other hand, the values of $\delta\sigma$ in Table 2 show that the converse need not be true. At the point of zero charge, the solvent dipoles are subjected to the field of a residual charge which can produce orientation. The charge density σ_M for which the total electric field at the dipoles, $z = \frac{1}{2}(d_1 + d_2)$, vanishes is somewhat negative (by about $0.4 \mu\text{C}/\text{cm}^2$) relative to the point of zero charge: various estimates for this charge density have been made [1]. There is agreement on the negative sign, but magnitudes vary from several tenths of a $\mu\text{C}/\text{cm}^2$ to several $\mu\text{C}/\text{cm}^2$. The effect of the delocalization of metal electrons, as represented by $\delta\sigma$, becomes of minor importance where σ deviates from zero by several $\mu\text{C}/\text{cm}^2$ or more in either direction.

(3) Influence of the Distance d_1

It will be noted that the distance d_1 between the jellium edge and the dielectric film is of primary importance in our model. It represents a transition zone for the electrons, whose width should differ for different metals; we have used the metal crystallographic radius for d_1 . A more complete model for the interface would [End of page 29] include the forces (electrostatic, van der Waals, closed-shell repulsions, etc.) between the solvent molecules and the metal ion cores, and predict the distance $\frac{1}{2}(d_1 + d_2)$ between the last plane of metal ions and the centers of the adsorbed solvent molecules. This distance, like d_1 , should depend on the metal, but also on the state of charge of the interface. One can imagine that the occupation of the antibonding orbitals which accept metal electrons increases with the number of electrons available (σ_M increasingly negative). Alternatively, increased screening of the ion charges should reduce attraction between ionic and molecular cores. Either way, the effective ion-molecule attraction should increase as σ_M increases, so that the average value of d_1 should decrease. Because of the importance of this parameter [5], we have considered the influence of such an effect on the capacity C^* of our model.

The simplest assumption for the variation of d_1 with charge is a linear relationship: $d_1 = R_c - \mu\sigma_M$ with μ positive. Given a value for the slope μ , one can obtain d_1 for each value of σ_M , recalculate α and β , and obtain electrical properties such as C^* . In Table 3 we present C^* as a function of σ_M for $\mu = 0$ and $\mu = R_c/80$. The solvent polarisation (P) has not been considered in these calculations. It can be seen that the effect of μ can be relatively important, especially for positive σ_M , for which d_1 becomes small. The capacity as a function of σ_M becomes almost constant although its value is not much changed near the point of zero charge.

Clearly, one would like a treatment of the entire interface, including simultaneously metal and electrolyte. The electrostatic and short-range interactions between particles would then determine, for a given state of charge, parameters such as d_1 . Such a treatment being beyond our means at present, one can only hope to treat separately different aspects of the system, and elucidate which effects are likely to be important. For example, a point dipole model of the solvent shows that non-interacting, freely orienting dipoles do not suffice to explain the behavior of water in the polarisable interface, but that adsorption and association must be introduced [1]. The work discussed here indicates that the electrons of the metal make an important contribution to the capacitance of the interface, and that the coupling between the metal and the solvent is small enough to permit separate modeling of one phase or the other. In such a treatment one can show the effect on interfacial properties of the parameters of the model, as we have done for d_1 in this section and for other parameters in preceding work.

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